

# Effect of Yb Addition on the Sintering Behavior and High Power Piezoelectric Properties of $\text{Pb}(\text{Zr,Ti})\text{O}_3\text{-Pb}(\text{Mn,Nb})\text{O}_3$

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## Abstract

0.9 $\text{Pb}(\text{Zr}_{0.61}\text{Ti}_{0.39})\text{-0.1Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  piezoelectric ceramics doped with  $\text{Yb}_2\text{O}_3$  were prepared by conventional ceramic processing, and the effects of the Yb doping on the sintering behavior and high power piezoelectric properties were investigated. XRD measurements indicated that the piezoelectric ceramics with  $\text{Yb}_2\text{O}_3$  in this study were a single phase of polycrystalline perovskite. The sintering density was strongly affected by small amount of  $\text{Yb}_2\text{O}_3$  addition. Vibration velocity, which is one of the most important factors for high power piezoelectric applications, as high as 1.0 m/s (rms value), was obtained from the 0.2 mol%  $\text{Yb}_2\text{O}_3$  doped sample. This value is about 2.5 times higher than that for commercialized hard PZT ceramics.

## 1. Introduction

High power piezoelectric ceramics are applied to various devices, such as ultrasonic motors and piezoelectric transformers, as materials which can convert electrical energy to mechanical energy or vice versa at the electromechanical resonance. For these applications, piezoelectric ceramics exhibiting a high vibration velocity are used. Because the vibration velocity is represented in proportion to the product of electromechanical coupling factor  $k$  and mechanical quality factor  $Q_m$ , materials with a large electromechanical coupling factor and a large mechanical quality factor are used. The best examples of such high power piezoelectric ceramics are compositions comprising of  $\text{PbZrO}_3\text{-PbTiO}_3\text{-Pb}(\text{Sb}_{1/3}\text{Mn}_{2/3})\text{O}_3$  (PZT-PSM)<sup>1-3)</sup> and  $\text{PbZrO}_3\text{-PbTiO}_3\text{-Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PZT-PMnN).<sup>4)</sup>

Ise *et al.* reported the high power characteristics of PZT-PMnN piezoelectric system. This system showed very high vibration velocity compare to hard PZT and commercial PZT-PSM system.<sup>4)</sup> Recently, Gao *et al.* reported the combinatory effect of rare earth element doping on the piezoelectric properties of PZT-PSM system.<sup>1)</sup> By doping rare earth element such as  $\text{Yb}^{+3}$  or  $\text{Eu}^{+3}$ , electromechanical coupling factor  $k$  (softening effect) and mechanical quality factor  $Q_m$  (hardening effect), both were improved. Therefore the longitudinal vibration velocity of the samples was dramatically improved.

In this study, the effect of  $\text{Yb}_2\text{O}_3$  addition on the sintering behavior and the high power piezoelectric characteristics (especially vibration velocity) of PZT-PMnN system are described. It is expected that the combinatory 'hard' and 'soft' piezoelectric characteristics can be introduced for this system when rare earth elements are doped as in the previous studies. Accordingly, very high vibration velocity is expected from this system, because the vibration velocity of piezoelectric element is strongly related with electromechanical coupling factor and mechanical quality factor.

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## II. Experimental Procedure

Conventional ceramic processing by using reagent grade oxide powders was conducted to prepare the samples. Pellets ( $12.7 \times 3$  mm) and rectangular bars ( $15 \times 50 \times 3$  mm) were fabricated. Pressureless sintering of the ceramics is performed in a high purity alumina crucible at 1000 to 1200 °C for 2 hours. Apparent sintered densities were measured by the Archimedes method with Xylene ( $\rho = 0.861 \text{ g/cm}^3$  at 20 °C). Dielectric properties were obtained by measuring the capacitance and loss using an LCR meter (HP model 4284). To determine  $T_c$ , capacitance measurements were made as a function of temperature in an automated temperature controlled furnace interfaced with a computer for data acquisition. The piezoelectric coefficient  $d_{33}$  was recorded from one-day aged samples using a Berlincourt-d33 meter (IAAS ZJ-2, Beijing, China). The electromechanical coupling factor  $k_p$  and mechanical quality factor  $Q_m$  were measured using an impedance analyzer (Model HP 4194) based on the IEEE standards. The vibration velocity  $v_o$  was measured using laser doppler vibrometers (LDV) Model OFV-3001 and OFV-511 (Polytec PI). The 4-pt flexural strength ( $\sigma_f$ ) was measured with an universal testing machine (AG-500E, Shimadzu Co., Japan). Fracture toughness ( $K_{IC}$ ) was determined with the IS (indentation strength) method using Vickers hardness tester (DVK-2S, Matsuzawa Co., Ltd., Japan) and universal testing machine.

## III. Results and discussion

Figure 1 shows the XRD patterns of PZT-PMnN ceramics with several  $\text{Yb}_2\text{O}_3$  contents of 0 (a), 0.2 (b), 0.5 (c), and 1.0 (d) mol%. All the peaks are assigned to rhombohedral perovskite structure. This indicates that the ceramics with  $\text{Yb}_2\text{O}_3$  shown above are a single phase of polycrystalline PZT-PMnN perovskite.

Figure 2 shows apparent sintered density as a function of sintering temperature for PZT-PMnN ceramics with several  $\text{Yb}_2\text{O}_3$  contents. All samples were sintered for 2 hours at each temperature. With increasing sintering temperature, the density is increased gradually. For the samples with 0.2 and 0.5 mol%  $\text{Yb}_2\text{O}_3$ , the density is saturated and fully dense at around 1100 °C. While this ceramics are expected to be especially useful in multilayered transformers, sintering temperature of 1100 °C would be preferred for multilayer designs because of relatively low cost metals, such as low Pd-fraction Ag-Pd alloys, could be employed for the internal electrodes.<sup>5)</sup>

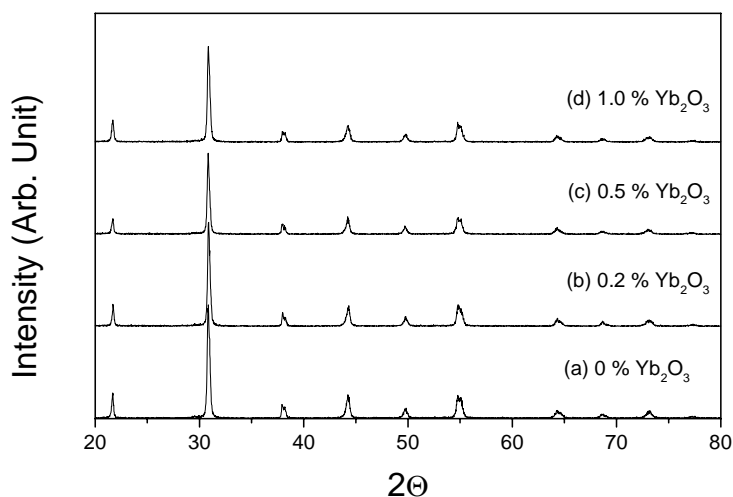


Fig. 1. XRD patterns of PZT-PMnN sintered body with  $\text{Yb}_2\text{O}_3$  content of (a) 0, (b) 0.2, (c) 0.5, and (d) 1.0 mol%. All samples are sintered at 1200 °C for 2 h.

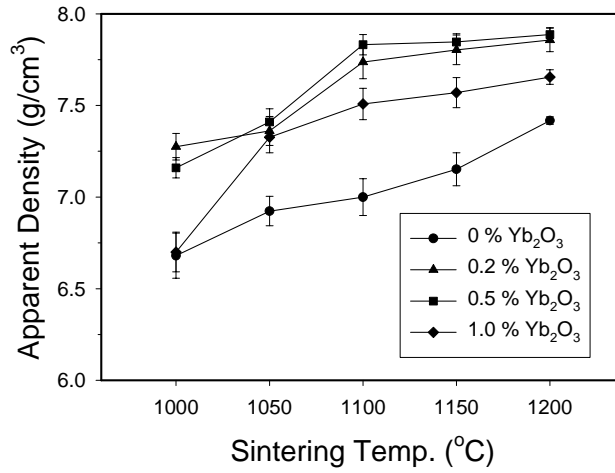


Fig. 2. Apparent density as a function of sintering temperature.

The fracture surfaces of samples sintered at 1200 °C for 2 hours were examined by SEM and showed in Fig. 3. The doping of Yb<sub>2</sub>O<sub>3</sub> has significant influences on the microstructure of PZT-PMnN ceramics. When pure PZT-PMnN was heated to 1200°C for 2 hours, it shows liquid phase on the microstructure. Contrary to this, the microstructures of doped with Yb<sub>2</sub>O<sub>3</sub> are quite different from that of pure PZT-PMnN. When the Yb<sub>2</sub>O<sub>3</sub> added compositions were sintered at the same condition, liquid phase was not existing and it seems to be perfect solid state sintered microstructure. And the sinterability of the composite is improved as illustrated in Fig. 2. When Yb<sub>2</sub>O<sub>3</sub> is added to PZT-PMnN as a solid solution, point defects might be created, and the created point defect might be the reason of the suppression of liquid phase during sintering.

Figure 4 shows the temperature dependence of the dielectric constant and loss at 1 kHz. The room temperature dielectric constant and loss were almost constant with changing Yb<sub>2</sub>O<sub>3</sub> doping content. The temperature of the dielectric constant maximum (Curie Temperature, T<sub>c</sub>), which is the effective phase transition temperature, is not changed either and the values were in the range of 305 ~ 310 °C, which is high enough for high power piezoelectric applications such as piezo-transformers and piezoelectric ultrasonic motors. The Curie temperature is one of important properties for high power piezoelectric applications. During high power operation, generated heat may cause the de-polarization of the piezoelectric. If the Curie temperature of the piezoelectric materials is not high enough, performance of piezoelectric devices can be dramatically degraded because of de-poling and temperature dependence of piezoelectric properties.

Piezoelectric properties and mechanical properties are summarized in table 1. The piezoelectric properties are obtained from impedance curve under driving voltage of 0.5 V<sub>p-p</sub>. As the amount of Yb<sub>2</sub>O<sub>3</sub> dopant increased from 0 to 0.5 mol%, electromechanical coupling factor (k<sub>p</sub>) increased by 17%, and the absolute value of piezoelectric constant (d<sub>33</sub>) decreased from 110 to 105 pC/N, however, the change of d<sub>33</sub> is negligible.

Table 1 also shows that the mechanical quality factor (Q<sub>m</sub>) of Yb<sub>2</sub>O<sub>3</sub> added PZT-PMnN decreased from 2200 to 540 as the amount of Yb<sub>2</sub>O<sub>3</sub> addition increased from 0 to 1.0 mol%.

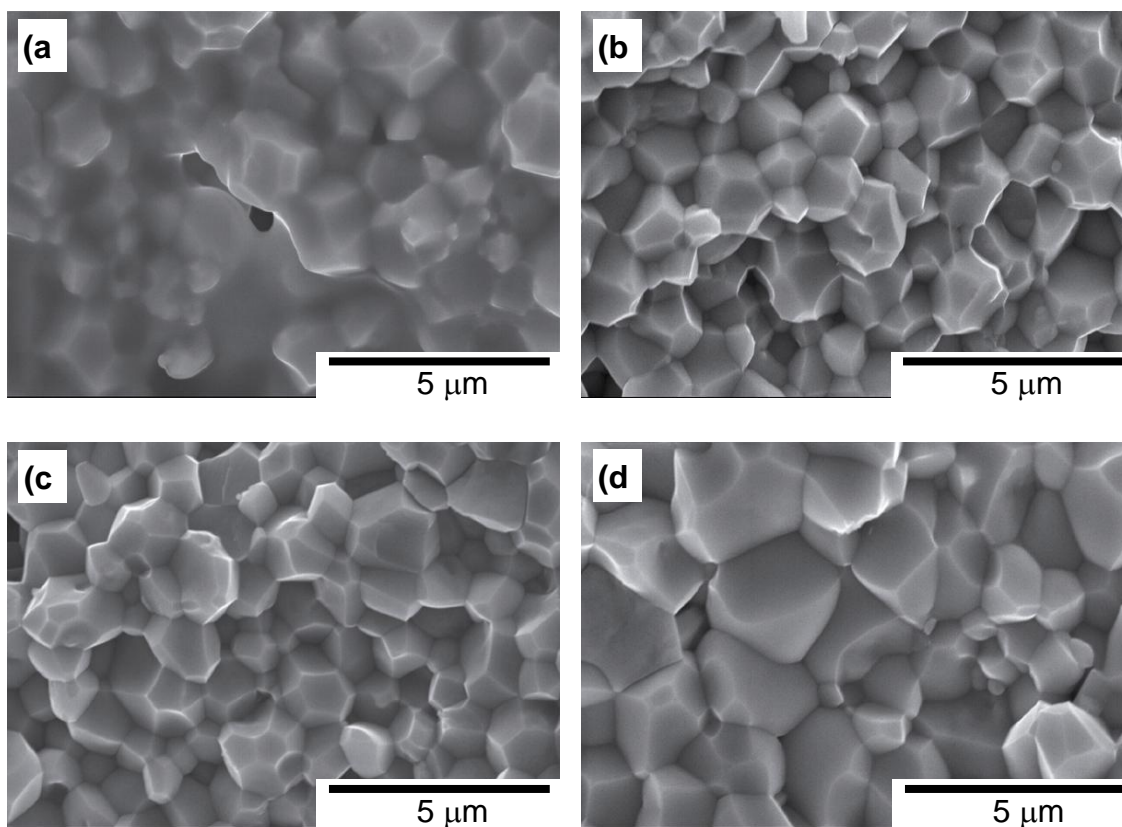


Fig. 3. SEM micrographs of fracture surfaces of sintered body. (a) 0, (b) 0.2, (c) 0.5, and (d) 1.0 mol%  $\text{Yb}_2\text{O}_3$  doped sample sintered at  $1200^\circ\text{C}$  for 2 hours

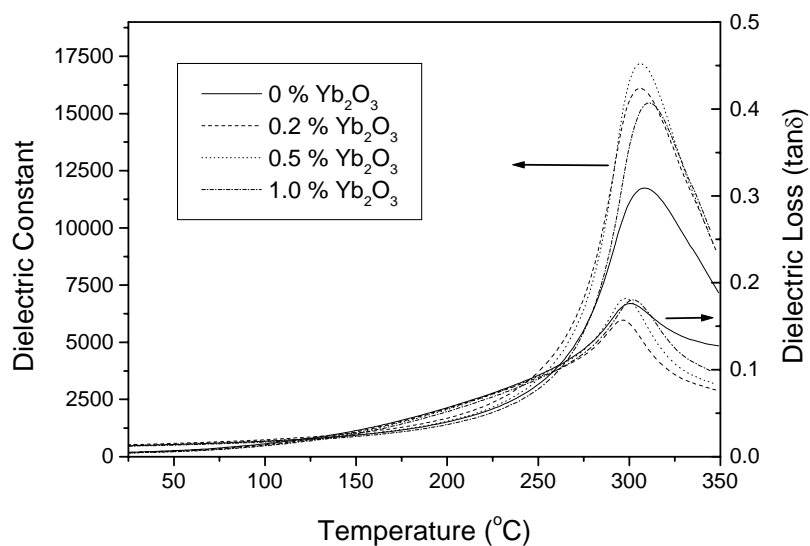


Fig. 4. (a) Dielectric constant and (b) dielectric loss as function of temperature for PZT-PMnN with various  $\text{Yb}_2\text{O}_3$  doping concentrations. All samples were sintered at  $1200^\circ\text{C}$  for 2 hours.

Table 1. Dielectric and piezoelectric properties of PZT-PMnN with changing  $\text{Yb}_2\text{O}_3$  doping content. Samples are sintered at 1200 °C for 2 hours.

$\text{Yb}_2\text{O}_3$ (mol%)	Density ( $\text{g/cm}^3$ )	$T_c$ (°C)	$k_p$	$\varepsilon_3^T/\varepsilon_0$	$\tan \delta$	$d_{33}$ (pC/N)	$Q_m$	$V_{\max}$ (m/s)	$\sigma_f$ (MPa)	$K_{IC}$ ( $\text{MPam}^{1/2}$ )
0.0	7.55	309	0.333	350	0.014	110	2200	0.79	$84 \pm 5$	$1.23 \pm 0.12$
0.2	7.85	306	0.382	365	0.023	108	1100	1.00	$121 \pm 6$	$1.43 \pm 0.16$
0.5	7.85	306	0.389	340	0.007	105	850	0.96	$114 \pm 5$	$1.38 \pm 0.18$
1.0	7.63	310	0.355	330	0.007	104	540	0.95	$94 \pm 7$	$1.33 \pm 0.13$

For practical piezoelectric devices, mechanical properties such as fracture strength ( $\sigma_f$ ) and fracture toughness ( $K_{IC}$ ) are important in the viewpoint of reliability. The samples with  $\text{Yb}_2\text{O}_3$  addition, the mechanical properties are higher than those of undoped samples. The superior mechanical properties of 0.2 and 0.5 mol%  $\text{Yb}_2\text{O}_3$  doped samples are mainly due to higher density and finer grain size. Since the fracture mode of specimens is intergranular fracture, the lower content of liquid phase (or solid state sintering) of the specimen with  $\text{Y}_2\text{O}_3$  can be the other reason of superior mechanical properties.

Figures 5 and 6 show vibration velocity ( $v_o$ , rms value) as a function of the electric field ( $E_{ac}$ , rms value) and temperature rise as a function of vibration velocity of the samples, respectively. With increasing  $E_{ac}$ , saturation in the value of  $v_o$  started and the value was higher than 0.95 m/s for the  $\text{Yb}_2\text{O}_3$  added samples.

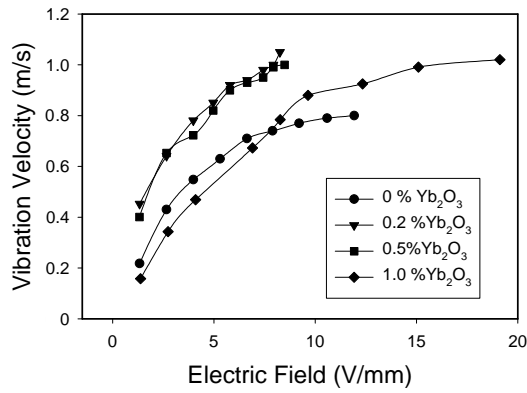


Fig. 5. Vibration velocity ( $v_o$ ) as a function of applied electric field ( $E_{ac}$ ).

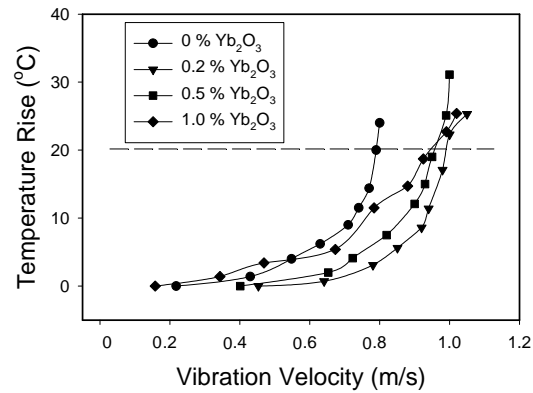


Fig. 6. Temperature rise as a function of vibration velocity.

This saturation was due to a decrease in mechanical quality factor  $Q_m$  with increasing  $E_{ac}$  above a critical vibrational level, as well as heat generation. The vibration velocity is related with the piezoelectric constant ( $d$ ), permittivity ( $\varepsilon$ ), elastic compliance ( $s$ ), electro-mechanical coupling factor ( $k$ ), and mechanical quality factor ( $Q_m$ ).<sup>6)</sup> Since the piezoelectric properties shown in table 1 were obtained under very low electric field ( $< 0.2$  V/mm), the vibration velocity in the fig. 5 is not directly proportional to those piezoelectric properties. Therefore the samples with 0 and 1 mol%  $\text{Yb}_2\text{O}_3$  could show lower vibration velocity at the electric field of 1-2 V/mm, even there is no temperature rise (fig. 6). It is well known that high  $Q_m$

values can be dramatically decreased above certain critical high electric field driving level (or vibration velocity).<sup>6,7)</sup> The mechanical quality factor of the sample with 0 mol%  $\text{Yb}_2\text{O}_3$  might be changed significantly at the electric field level of 1-2 V/mm. At  $E_{ac} \sim 8.5$  V/mm (rms value),  $v_o$  was found to be as high as 1.0 m/s (rms value) for a sample with 0.2 and 0.5 mol%  $\text{Yb}_2\text{O}_3$  doped samples. These high vibration velocity values are around 2.5 times higher than that of the conventional hard PZT ceramic which had a value of around 0.40 m/s (rms value) at the higher  $E_{ac}$  drive level.<sup>6)</sup> The maximum vibrational velocity,  $v_{max}$  (at temperature rise  $\Delta T = 20^\circ\text{C}$ ), for 0.2 mol%  $\text{Yb}_2\text{O}_3$  doped sample was found to be 1.0 m/s, which is higher than that of PZT-PSM with Yb or Er doped composition which shows very high vibration velocity, reported by Gao et al.<sup>1)</sup> and other high vibration velocity piezoelectric materials. It is expected that this exceptionally high vibration velocity can generate more power and convert electric energy. PZT-PMnN- $\text{Yb}_2\text{O}_3$  piezoelectric materials can be utilized for high power piezoelectric devices such as piezoelectric transformers and ultrasonic motors.

#### IV. Conclusion

The dielectric and piezoelectric characteristics were investigated for the  $0.9\text{Pb}(\text{Zr}_{0.61}\text{Ti}_{0.39})-0.1\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{Yb}_2\text{O}_3$  system ( $0 < x < 0.01$ ). Addition of  $\text{Yb}_2\text{O}_3$  was effective for improving high power piezoelectric characteristics such as vibration velocity of PZT-PMnN system. Curie temperature was high enough and did not change with  $\text{Yb}_2\text{O}_3$  doping and the value was around  $310^\circ\text{C}$ . High vibration velocity ( $v_o$ ) were improved from 0.79 m/s to 1.0 m/s by doping of 0.2 mol%  $\text{Yb}_2\text{O}_3$ . This value is exceptionally higher than commercial hard PZT piezoelectric ceramics. The mechanical strength and fracture toughness of  $\text{Yb}_2\text{O}_3$  doped samples higher than those of undoped samples and the values were 121 MPa and  $1.43 \text{ MPam}^{1/2}$ . It is expected that this piezoelectric material can be utilized for high power piezoelectric devices such as piezoelectric transformers and ultrasonic motors.

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